

PATENT ABSTRACTS OF JAPAN

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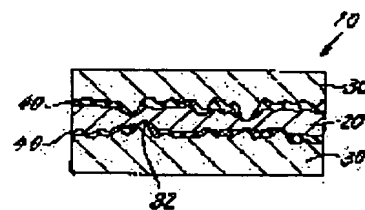
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(54) CELL FOR SOLID HIGH POLYMER TYPE FUEL CELL AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To attain the thinning of a solid electrolyte film while avoiding the generation of pinhole and provide a cell operable under non-humidification by forming an electrolyte layer consisting of an electrolyte material between a catalyst layer and the solid electrolyte film.

SOLUTION: A cell for solid polymer type fuel cell 10 comprises an electrolyte layer 40 consisting of an electrolyte material, which is formed between a catalyst layer 30 and a solid electrolyte film 20. The electrolyte layer 40 is desirably formed of the same component as the solid electrolyte film 20, and the thickness of the electrolyte layer 40 is desirably thinner than the solid electrolyte film 20. The electrolyte layer 40 is formed on the catalyst layer 40 on the connecting side with the solid electrolyte film 20. The total thickness of the solid electrolyte film 20 and the electrolyte layer 40 connected to one surface or both surfaces of the solid electrolyte film 20 is desirably set to 5-50 μm . The electrolyte layer 40 can be formed by arranging the catalyst layer 30 and the sheet-like electrolyte material one over another followed by heating and pressurizing.



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CLAIMS

[Claim(s)]

[Claim 1] The cel for the quality type fuel cells of a solid-state macromolecule characterized by forming the electrolyte layer (40) which consists of an electrolyte ingredient between a catalyst bed (30) and a solid-electrolyte membrane (20) in the cel for polymer electrolyte fuel cells which comes to arrange a catalyst bed (30) on the surface of a solid-electrolyte membrane (20).

[Claim 2] The sum total thickness of an electrolyte layer (40) and a solid-electrolyte membrane (20) is 5-micrometer or more a cel for the quality type fuel cells of a solid-state macromolecule according to claim 1 which is 50 micrometers or less.

[Claim 3] In the production approach of the cel for polymer electrolyte fuel cells which comes to join a catalyst bed (30) on the surface of a solid-electrolyte membrane (20) The electrolyte layer (40) which consists of an electrolyte ingredient is formed in the catalyst bed (30) side by the side of junction to a solid-electrolyte membrane (20). The production approach of the cel for polymer electrolyte fuel cells characterized by joining the electrolyte layer (40) and solid-electrolyte membrane (20) which were formed in the catalyst bed (30) by performing heating and application of pressure.

[Claim 4] An electrolyte layer (40) is the production approach of the cel for the quality type fuel cells of a solid-state macromolecule according to claim 3 which pressurizes with heating and is formed after arranging the electrolyte ingredient of the shape of a catalyst bed (30) and a sheet in piles.

[Claim 5] The process which forms an electrolyte layer (40) on a catalyst bed (30) is the production approach of the cel for the quality type fuel cells of a solid-state macromolecule according to claim 4 carried out by applying 30kg/cm² or more the pressure of 500kg/cm² or less under the temperature of under decomposition temperature more than the glass transition temperature of an electrolyte ingredient.

[Claim 6] The process which forms an electrolyte layer (40) on a catalyst bed (30) is the production approach of the cel for the quality type fuel cells of a solid-state macromolecule according to claim 4 carried out by applying 150kg/cm² or more the pressure of 400kg/cm² or less under the temperature of under decomposition temperature more than the glass transition temperature of an electrolyte ingredient.

[Claim 7] An electrolyte layer (40) is the production approach of the cel for the quality type fuel cells of a solid-state macromolecule according to claim 3 formed by carrying out the plasma polymerization of the electrolyte ingredient on the surface of a catalyst bed (30).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] About the cel which consists of a solid-electrolyte membrane used for the quality type fuel cell of a solid-state macromolecule, and a catalyst bed, this invention can specifically attain thin film-ization of a solid-electrolyte membrane, and relates to the cel in which no humidifying can also operate.

[0002]

[Description of the Prior Art] The quality type fuel cell of a solid-state macromolecule (70) consists of units whose cels (10) by which the electrode (a fuel electrode (72) and air pole (75)) was formed in both sides of the solid-electrolyte membrane (20) to which it is ion conductivity and a proton is moved were pinched by the combustion chamber by the side of a fuel electrode (73), and the oxidizer room by the side of an air pole (76), as shown in drawing 5. The hydrogen rich fuel gas which reformed methane, town gas, etc. is supplied to the combustion chamber (73) of a unit, and the oxidant gas containing oxygen, such as air, is supplied to an oxidizer room (76). In a fuel electrode (72), a proton and an electron are generated by the reaction of $H_2 \rightarrow 2H^{++} + 2e^-$, and, as for an electron, a proton flows [the hydrogen gas in fuel gas] to an external circuit (78) toward an air pole (75) through a solid-electrolyte membrane (20) by it. In an air pole (75), by the reaction of $1/2O_2 + 2H^{++} + 2e^- \rightarrow H_2O$, the oxygen in oxidant gas, the proton which moved through the solid-electrolyte membrane (20), and the electron which flowed through the external circuit (78) generate electromotive force, while producing water.

[0003] The electrode (72) formed on the surface of a solid-electrolyte membrane and (75) are constituted by the porous catalyst bed (30) which was made to support catalyst ingredients, such as Pt, into conductive ingredients, such as a carbon particle, and generally fabricated them into them. As for the reaction of distributed gas, the interface in which an electrolyte ingredient, a conductive ingredient, and a catalyst ingredient exist simultaneously serves as a reacting point. For this reason, many reacting points are made to exist on a cel, and it becomes important for acceleration of a reaction to make an electrolyte ingredient, a conductive ingredient, and a catalyst ingredient connect by network. Then, the cel was conventionally produced by carrying out a hotpress on both sides of a solid-electrolyte membrane between the catalyst beds which consist of a conductive ingredient and a catalyst ingredient.

[0004] It depends for the ion conductivity of a solid-electrolyte membrane on the moisture concentration in an ambient atmosphere, and the thickness of a solid-electrolyte membrane remarkably. If the moisture concentration in an ambient atmosphere is low, membrane resistance will increase and ion conductivity will fall. However, in order to carry out humidity of the film, the means for humidification, such as humidifying distributed gas, is needed, and it leads to enlargement of the quality type fuel cell of a solid-state macromolecule, and decline in generation efficiency. On the other hand, if thickness of a solid-electrolyte membrane is made thin, the moisture transfer in the film can become easy and it can be made to operate by low humidification or no humidifying. Moreover, membrane resistance can become small and can raise a cel electrical potential difference. For this reason, thin film-ization of a solid-electrolyte membrane is advanced.

[0005]

[Problem(s) to be Solved by the Invention] When realizing thin film-ization of a solid-electrolyte membrane and the hotpress was performed on both sides of the thin solid-electrolyte membrane 50 micrometers or less between catalyst beds, as shown in drawing 6, the solid-electrolyte membrane (20) was broken through by the irregularity of the front face of a catalyst bed (30), and the pinhole (80) might occur with it. A solid-electrolyte membrane (20) must play the role which prevents fuel gas and oxidant gas blending while

permitting migration of a proton. However, if a pinhole is in a solid-electrolyte membrane (20), it becomes easy to leak distributed gas and is not desirable. In addition, the fuel electrode and the air pole short-circuited through the pinhole, and it had also become the cause which causes the degradation of a cell. In order to prevent generating of a pinhole etc., when the conditions of a hotpress were weakened, the problem it becomes inadequate connecting [of a catalyst bed (30) and a solid-electrolyte membrane (20)] by network was in reverse.

[0006] The object of this invention is avoiding a pinhole, being able to attain thin film-ization of a solid-electrolyte membrane, and offering the cell for the quality type fuel cells of a solid-state macromolecule in which no humidifying can also operate.

[0007]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the cell for the quality type fuel cells of a solid-state macromolecule of this invention (10) forms the electrolyte layer (40) which consists of an electrolyte ingredient between a catalyst bed (30) and a solid-electrolyte membrane (20). As for an electrolyte layer (40), it is desirable to form from the same component as a solid-electrolyte membrane (20), and it is [the thickness of an electrolyte layer (40)] desirable to make it thinner than a solid-electrolyte membrane (20). An electrolyte layer (40) is formed in the field of the catalyst bed (30) by the side of junction to a solid-electrolyte membrane (20). As an approach of forming an electrolyte layer (40), after arranging a catalyst bed (30) and a sheet-like electrolyte ingredient in piles, the approach of performing heating and application of pressure can be mentioned. Moreover, the approach of carrying out the plasma polymerization of the electrolyte ingredient on the surface of a catalyst bed (30) can be mentioned as an option which forms an electrolyte layer (40). After forming an electrolyte layer (40) in a catalyst bed (30), the electrolyte layer (40) and solid-electrolyte membrane (20) on a catalyst bed (30) are joined by heating and application of pressure, and the cell for the quality type fuel cells of a solid-state macromolecule (10) is produced.

[0008]

[Function and Effect] An electrolyte layer (40) can be beforehand formed in a catalyst bed (30), a solid-electrolyte membrane (20) can be joined on the application-of-pressure conditions that it is weak when joining a solid-electrolyte membrane (20) to the catalyst bed (30) in which the electrolyte layer (40) was formed, since the interface in which an electrolyte ingredient, a conductive ingredient, and a catalyst ingredient exist simultaneously is formed, and a solid-electrolyte membrane (20) is not broken through by the catalyst bed (30). That is, breakage on a solid-electrolyte membrane (20) can be prevented, forming many interfaces which consist of an electrolyte ingredient, a conductive ingredient, and a catalyst ingredient. Since a solid-electrolyte membrane (20) does not receive breakage, even if it thin-film-izes a solid-electrolyte membrane (20), leak or an electric short circuit of gas do not arise. Moreover, the actuation under the ambient atmosphere where it does not humidify also becomes possible by attaining thin film-ization of a solid-electrolyte membrane (20). Even if a solid-electrolyte membrane (20) or an electrolyte layer (40) receives breakage, the electrolyte layer (40) by the side of a catalyst bed (30) has covered the solid-electrolyte membrane (20) top, and since a solid-electrolyte membrane (20) and the breakage location of an electrolyte layer (40) are not in agreement, penetration of a pinhole will not take place.

[0009]

[Embodiment of the Invention] One operation gestalt of the production approach of the cell for the quality type fuel cells of a solid-state macromolecule of this invention is explained. First, the following solid-electrolyte membranes, catalyst beds, and electrolyte layers are prepared.

A solid-electrolyte membrane solid-electrolyte membrane can be formed from electrolyte ingredients, such as perfluorocarbon sulfonic acid and a styrene-divinylbenzene sulfonic acid. As for the thickness of a solid-electrolyte membrane, it is desirable to be referred to as 5 micrometers - 40 micrometers. Moreover, the magnitude of a solid-electrolyte membrane can be suitably chosen to compensate for the engine performance of the quality type fuel cell of a solid-state macromolecule produced. In addition, since it is necessary to make thickness of an electrolyte ingredient thin to operate the quality type fuel cell of a solid-state macromolecule by no humidifying, it is desirable to set to 5 micrometers or more 50 micrometers or less sum total thickness with the electrolyte layer joined by one side or both sides of a solid-electrolyte membrane and a solid-electrolyte membrane.

A catalyst bed catalyst bed can be formed with the sheet metal of the porosity which fabricated with the binder etc. the powder which made conductive ingredients, such as carbon of 10 micrometers - 70 micrometers of mean diameters, support catalyst ingredients, such as mean-diameter 10micrometer-300A Pt and Ru (ruthenium), with sintering, rolling, etc. 10 micrometers - about 100 micrometers are suitable for

the thickness of a catalyst bed, and it is processed into magnitude [a little] smaller than the solid-electrolyte membrane joined.

As for an electrolyte layer electrolyte layer, it is desirable to form from the electrolyte ingredient of the same component as a solid-electrolyte membrane. When forming an electrolyte layer in a catalyst bed by heating and application of pressure of a hotpress etc., it is desirable to form an electrolyte ingredient beforehand with a thickness of 1 micrometer - 10 micrometers in the shape of a sheet.

[0010] Formation of the electrolyte layer to a catalyst bed can join a sheet-like electrolyte ingredient to the piece side face of a catalyst bed by giving heating and application of pressure in piles. As the junction approach, a hotpress is applicable. In addition, an electrolyte layer can be formed also by the plasma polymerization as the following examples explain it. More than the glass transition temperature of an electrolyte ingredient, it is appropriate for junction of a catalyst bed and an electrolyte ingredient under the temperature of under decomposition temperature to carry out by applying 30kg/cm² or more the pressure of 500kg/cm² or less, and it is desirable to carry out by 150kg/cm² or more the pressure of 400kg/cm² or less. Drawing 2 is the enlarged drawing showing a part for the joint of a catalyst bed (30) and an electrolyte layer (40). It turns out as a graphic display that an electrolyte ingredient (42) invades between the conductive powder (34) with which catalyst powder (32) was supported, and it is connected by network.

[0011] About a solid-electrolyte membrane (20), it inserts in between so that the electrolyte layer side of a catalyst bed (30) may counter with a solid-electrolyte membrane (20), and heating and application of pressure are given and an electrolyte layer (40) and a solid-electrolyte membrane (20) are joined to the catalyst bed (30) of the couple in which the electrolyte layer (40) was formed (refer to drawing 1). A hotpress can be mentioned as the junction approach. Heating and application-of-pressure conditions can be made into 5kg/cm² or more the pressure of 30kg/cm² or less under the temperature of under decomposition temperature more than the glass transition temperature of an electrolyte ingredient. That what is necessary is just to join an electrolyte layer and a solid-electrolyte membrane so that it may not separate during actuation, since it is not necessary to connect by network like junction in the above-mentioned catalyst bed and an electrolyte layer, a solid-electrolyte membrane can be joined on application-of-pressure conditions weaker than the application-of-pressure conditions which formation of an electrolyte layer took.

[0012] As mentioned above, an electrolyte layer is formed on the surface of a catalyst bed, and the cel for the quality type fuel cells of a solid-state macromolecule is produced by joining an electrolyte layer to a solid-electrolyte membrane. In addition, temporarily, at the time of junction in a catalyst bed and an electrolyte layer, with the irregularity of the front face of a catalyst bed (30), since the application-of-pressure conditions at the time of junction to the solid-electrolyte membrane (20) which is an after process also considering breakage (82) as a carrier beam in part are weak, as for a solid-electrolyte membrane (20), an electrolyte layer (40) does not receive breakage.

[0013]

[Example] The catalyst bed was produced in the following ways, the electrolyte layer was formed in the front face of the obtained catalyst bed, it joined to the solid-electrolyte membrane on the electrolyte layer, and the cel for the quality type fuel cells of a solid-state macromolecule (this invention cel) was produced. Moreover, for the comparison, it joined to the solid-electrolyte membrane at the catalyst bed which does not form an electrolyte layer, and the cel (reference cell) was produced. The single cel trial was carried out using the produced cel.

[0014] First, the production approach of a catalyst bed is explained.

After mixing and filtering CaCO₃ by making catalyst bed Pt support carbon into Binder PTFE (polytetrafluoroethylene) and an ostomy agent, it rolled out and fabricated in the shape of a sheet.

Subsequently, it was immersed into 1N-HNO₃, the ostomy agent was removed, and area 2 and the catalyst bed with a thickness of 50 micrometers of 25cm were formed as a porous sheet. Hereafter, all catalyst beds used what was obtained by this production approach.

[0015] The following cels (the invention cels 1-4 and reference cells 1 and 2) were produced using the obtained catalyst bed.

the sheet-like electrolyte ingredient (perfluorocarbon-sulfonic-acid film (Du Pont Nafion film), thickness: 5 micrometers) was joined to the front face of the production profit **** catalyst bed of the invention cel 1 with the hotpress under the temperature of 180 degrees C, and conditions with a pressure of 300kg/cm², and the electrolyte layer was produced. When a part for a joint was observed, the electrolyte layer (40) became the uneven shape of a sheet with a thickness of 1 micrometer - 5 micrometers, it welded (30), and some electrolyte ingredients (42) had trespassed upon the interior of a catalyst bed (30) (refer to drawing 2). Between one pair of catalyst beds in which the electrolyte layer was formed, the solid-electrolyte membrane

with a thickness of 40 micrometers it is thin from the same electrolyte ingredient as an electrolyte layer was inserted, the hotpress was carried out under the temperature of 150 degrees C, and conditions with a pressure of 10kg/cm², the solid-electrolyte membrane was joined to the electrolyte layer, and the invention cel 1 was produced.

Except having set to 10 micrometers thickness of the electrolyte layer joined to the production catalyst bed of the invention cel 2, the production approach is the same as the invention cel 1.

Except having set to 20 micrometers thickness of the electrolyte layer joined to the production catalyst bed of the invention cel 3, the production approach is the same as the invention cel 1.

By the production plasma polymerization of the invention cel 4, the electrolyte layer was formed on the surface of the catalyst bed. As plasma polymerization equipment (90) is shown in drawing 3, one side is connected to a high-frequency power generator (96), and the electrode plate (94) of a couple with which another side was grounded, and (95) are arranged, it is open for free passage to a chamber (93), and raw material charge tubing (97) is connected to the interior of the chamber (93) connected to the vacuum pump (92). Hexafluoropropylene and trifluoro methansulfonic acid were supplied as an electrolyte ingredient (42) from raw material charge tubing (97), having placed the catalyst bed (30) between an electrode plate (94) and (95), having deaerated the inside of a chamber (93) with the vacuum pump (92), and impressing the power of 5W between an electrode plate (94) and (95) by the high-frequency power generator (96). Thereby, the electrolyte membrane with a thickness of about 1.2 micrometers was formed on the surface of the catalyst bed (30). Among one pair of catalyst beds in which the electrolyte layer was formed, the solid-electrolyte membrane was joined by the same approach as the invention cel 1.

[0016] The solid-electrolyte membrane with a thickness of 40 micrometers was joined on the same hotpress conditions (the temperature of 150 degrees C, pressure of 10kg/cm²) as the invention cel 1, not forming an electrolyte layer in the production catalyst bed of a reference cell 1.

The production approach is the same as a reference cell 1 except having made the hotpress conditions of the production solid-electrolyte membrane of a reference cell 2 into the temperature of 150 degrees C, and the pressure of 300kg/cm².

[0017] The obtained invention cels 1-4 and reference cells 1 and 2 were pinched with the carbon paper which gave a water-repellent finish, respectively, and the single cel trial was performed. Trials are the O.C.V. measurement shown below and measurement of the cel electrical potential difference in current density 500 mA/cm², the test condition was not cell temperature [of 80 degrees C], fuel humidification temperature [of 80 degrees C], and oxidizer humidified, H₂ was used as fuel gas and air was used for it as oxidant gas. In addition, the fuel utilization rate made the oxidizer utilization factor 20% 50%.

[0018] When the electrical potential difference (open-circuit voltage: O.C.V.) of each cel when supplying only gas is measured in the condition of not adding the load, as shown in drawing 4, although the invention cels 1-4 and a reference cell 1 all show the high value, the reference cell 2 serves as a low value. Since this had the high application-of-pressure conditions when forming a solid-electrolyte membrane in a catalyst bed, the breakage on a pinhole etc. arises in a solid-electrolyte membrane, and it is considered to be because for leak or an electric short circuit of gas to have occurred. On the other hand, the invention cels 1-4 and a reference cell 1 are considered that there is no breakage in a solid-electrolyte membrane.

[0019] Next, when the cel electrical potential difference in current density 500 mA/cm² is measured, as shown in drawing 4, it turns out that the invention cels 1-4 show the high cel electrical potential difference compared with reference cells 1 and 2. It is because the cel electrical potential difference of reference cells 1 and 2 compared with the invention cels 1-4 and the solid-electrolyte membrane has received breakage as the above-mentioned [low one / a reference cell 2], and although there is no breakage in a solid-electrolyte membrane, since the application-of-pressure conditions of a solid-electrolyte membrane and a catalyst bed are weak, a reference cell 1 is because the network of an electrolyte ingredient and a catalyst bed is not fully performed. The invention cels 1-4 show the high cel electrical potential difference compared with reference cells 1 and 2, because the invention cel has joined the catalyst bed and the electrolyte layer beforehand and the network with an electrolyte ingredient and a catalyst bed is fully performed. Moreover, the junction to the catalyst bed and the solid-electrolyte membrane in which the electrolyte layer was formed is to carry out on weak application-of-pressure conditions, and for a solid-electrolyte membrane not to receive breakage. In addition, although the cel electrical potential difference is low compared with the invention cels 1, 2, and 4, the thickness of an electrolyte ingredient becomes thick and, as for the invention cel 3, only the part to which this thickened the electrolyte layer shows that oxidizer non-humidified operation is difficult. That is, in performing non-humidified operation, it understands the sum total thickness of an electrolyte layer and a solid-electrolyte membrane that it is desirable to make it thinner than 50 micrometers.

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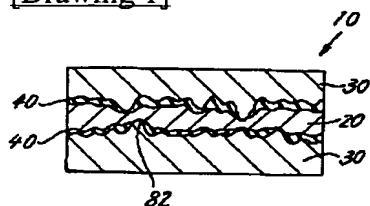
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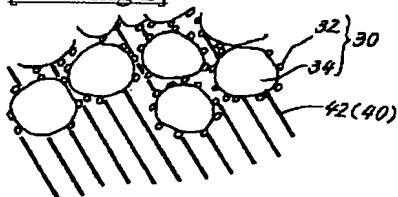
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DRAWINGS

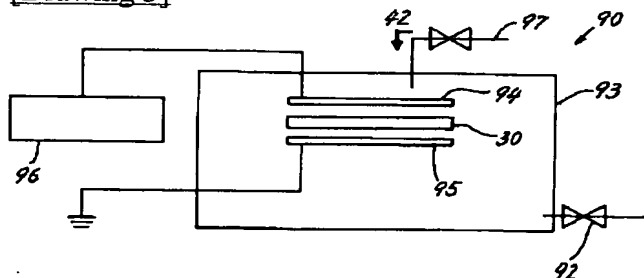
[Drawing 1]



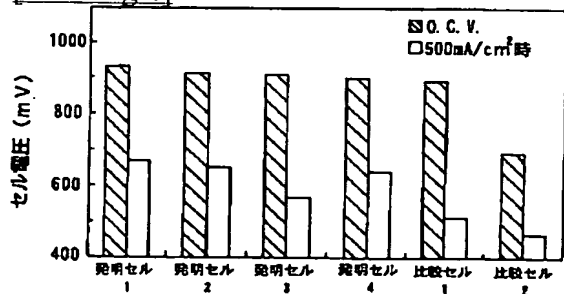
[Drawing 2]



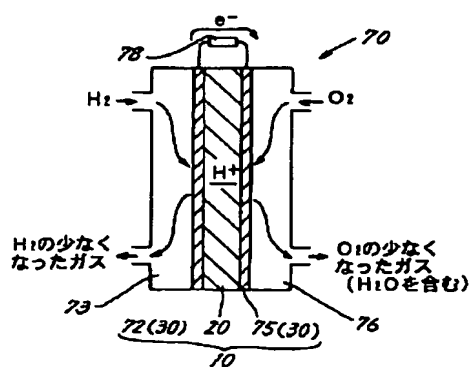
[Drawing 3]



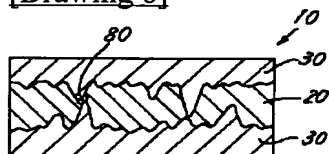
[Drawing 4]



[Drawing 5]



[Drawing 6]



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CORRECTION OR AMENDMENT

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[Procedure amendment]
 [Filing Date] September 13, Heisei 12 (2000. 9.13)
 [Procedure amendment 1]
 [Document to be Amended] Description
 [Item(s) to be Amended] Whole sentence
 [Method of Amendment] Modification
 [Proposed Amendment]
 [Document Name] Description
 [Title of the Invention] The cel for polymer electrolyte fuel cells, and its production approach
 [Claim(s)]
 [Claim 1] In the cel for polymer electrolyte fuel cells which comes to arrange a catalyst bed (30) on the surface of a solid-electrolyte membrane (20),
 The cel for polymer electrolyte fuel cells characterized by forming the electrolyte layer (40) which consists of an electrolyte ingredient between a catalyst bed (30) and a solid-electrolyte membrane (20).
 [Claim 2] The sum total thickness of an electrolyte layer (40) and a solid-electrolyte membrane (20) is 5-micrometer or more a cel for polymer electrolyte fuel cells according to claim 1 which is 50 micrometers or less.
 [Claim 3] In the production approach of the cel for polymer electrolyte fuel cells which comes to join a catalyst bed (30) on the surface of a solid-electrolyte membrane (20),
 The electrolyte layer (40) which consists of an electrolyte ingredient is formed in the catalyst bed (30) side by the side of junction to a solid-electrolyte membrane (20),
 The production approach of the cel for polymer electrolyte fuel cells characterized by joining the electrolyte layer (40) and solid-electrolyte membrane (20) which were formed in the catalyst bed (30) by performing heating and application of pressure.
 [Claim 4] An electrolyte layer (40) is the production approach of the cel for polymer electrolyte fuel cells

according to claim 3 which pressurizes with heating and is formed after arranging the electrolyte ingredient of the shape of a catalyst bed (30) and a sheet in piles.

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[Claim 7] An electrolyte layer (40) is the production approach of the cel for polymer electrolyte fuel cells according to claim 3 formed by carrying out the plasma polymerization of the electrolyte ingredient on the surface of a catalyst bed (30).

[Detailed Description of the Invention]

[0001]

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[0003] The electrode (72) formed on the surface of a solid-electrolyte membrane and (75) are constituted by the porous catalyst bed (30) which was made to support catalyst ingredients, such as Pt, into conductive ingredients, such as a carbon particle, and generally fabricated them into them. As for the reaction of distributed gas, the interface in which an electrolyte ingredient, a conductive ingredient, and a catalyst ingredient exist simultaneously serves as a reacting point. For this reason, many reacting points are made to exist on a cel, and it becomes important for acceleration of a reaction to make an electrolyte ingredient, a conductive ingredient, and a catalyst ingredient connect by network. Then, the cel was conventionally produced by carrying out a hotpress on both sides of a solid-electrolyte membrane between the catalyst beds which consist of a conductive ingredient and a catalyst ingredient.

[0004] It depends for the ion conductivity of a solid-electrolyte membrane on the moisture concentration in an ambient atmosphere, and the thickness of a solid-electrolyte membrane remarkably. If the moisture concentration in an ambient atmosphere is low, membrane resistance will increase and ion conductivity will fall. However, in order to carry out humidity of the film, the means for humidification, such as humidifying distributed gas, is needed, and it leads to enlargement of a polymer electrolyte fuel cell, and decline in generation efficiency. On the other hand, if thickness of a solid-electrolyte membrane is made thin, the moisture transfer in the film can become easy and it can be made to operate by low humidification or no humidifying. Moreover, membrane resistance can become small and can raise a cel electrical potential difference. For this reason, thin film-ization of a solid-electrolyte membrane is advanced.

[0005]

[Problem(s) to be Solved by the Invention] When realizing thin film-ization of a solid-electrolyte membrane and the hotpress was performed on both sides of the thin solid-electrolyte membrane 50 micrometers or less between catalyst beds, as shown in drawing 6, the solid-electrolyte membrane (20) was broken through by the irregularity of the front face of a catalyst bed (30), and the pinhole (80) might occur with it. A solid-electrolyte membrane (20) must play the role which prevents fuel gas and oxidant gas blending while permitting migration of a proton. However, if a pinhole is in a solid-electrolyte membrane (20), it becomes

easy to leak distributed gas and is not desirable. In addition, the fuel electrode and the air pole short-circuited through the pinhole, and it had also become the cause which causes the degradation of a cell. In order to prevent generating of a pinhole etc., when the conditions of a hotpress were weakened, the problem it becomes inadequate connecting [of a catalyst bed (30) and a solid-electrolyte membrane (20)] by network was in reverse.

[0006] The object of this invention is avoiding a pinhole, being able to attain thin film-ization of a solid-electrolyte membrane, and offering the cel for polymer electrolyte fuel cells in which no humidifying can also operate.

[0007]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the cel for polymer electrolyte fuel cells of this invention (10) forms the electrolyte layer (40) which consists of an electrolyte ingredient between a catalyst bed (30) and a solid-electrolyte membrane (20). As for an electrolyte layer (40), it is desirable to form from the same component as a solid-electrolyte membrane (20), and it is [the thickness of an electrolyte layer (40)] desirable to make it thinner than a solid-electrolyte membrane (20). An electrolyte layer (40) is formed in the field of the catalyst bed (30) by the side of junction to a solid-electrolyte membrane (20). As an approach of forming an electrolyte layer (40), after arranging a catalyst bed (30) and a sheet-like electrolyte ingredient in piles, the approach of performing heating and application of pressure can be mentioned. Moreover, the approach of carrying out the plasma polymerization of the electrolyte ingredient on the surface of a catalyst bed (30) can be mentioned as an option which forms an electrolyte layer (40). After forming an electrolyte layer (40) in a catalyst bed (30), the electrolyte layer (40) and solid-electrolyte membrane (20) on a catalyst bed (30) are joined by heating and application of pressure, and the cel for polymer electrolyte fuel cells (10) is produced.

[0008]

[Function and Effect] An electrolyte layer (40) can be beforehand formed in a catalyst bed (30), a solid-electrolyte membrane (20) can be joined on the application-of-pressure conditions that it is weak when joining a solid-electrolyte membrane (20) to the catalyst bed (30) in which the electrolyte layer (40) was formed, since the interface in which an electrolyte ingredient, a conductive ingredient, and a catalyst ingredient exist simultaneously is formed, and a solid-electrolyte membrane (20) is not broken through by the catalyst bed (30). That is, breakage on a solid-electrolyte membrane (20) can be prevented, forming many interfaces which consist of an electrolyte ingredient, a conductive ingredient, and a catalyst ingredient. Since a solid-electrolyte membrane (20) does not receive breakage, even if it thin-film-izes a solid-electrolyte membrane (20), leak or an electric short circuit of gas do not arise. Moreover, the actuation under the ambient atmosphere where it does not humidify also becomes possible by attaining thin film-ization of a solid-electrolyte membrane (20). Even if a solid-electrolyte membrane (20) or an electrolyte layer (40) receives breakage, the electrolyte layer (40) by the side of a catalyst bed (30) has covered the solid-electrolyte membrane (20) top, and since a solid-electrolyte membrane (20) and the breakage location of an electrolyte layer (40) are not in agreement, penetration of a pinhole will not take place.

[0009]

[Embodiment of the Invention] One operation gestalt of the production approach of the cel for polymer electrolyte fuel cells of this invention is explained. First, the following solid-electrolyte membranes, catalyst beds, and electrolyte layers are prepared.

Solid-electrolyte membrane

A solid-electrolyte membrane can be formed from electrolyte ingredients, such as perfluorocarbon sulfonic acid and a styrene-divinylbenzene sulfonic acid. As for the thickness of a solid-electrolyte membrane, it is desirable to be referred to as 5 micrometers - 40 micrometers. Moreover, the magnitude of a solid-electrolyte membrane can be suitably chosen to compensate for the engine performance of the polymer electrolyte fuel cell produced. In addition, since it is necessary to make thickness of an electrolyte ingredient thin to operate a polymer electrolyte fuel cell by no humidifying, it is desirable to set to 5 micrometers or more 50 micrometers or less sum total thickness with the electrolyte layer joined by one side or both sides of a solid-electrolyte membrane and a solid-electrolyte membrane.

Catalyst bed

A catalyst bed can be formed with the sheet metal of the porosity which fabricated with the binder etc. the powder which made conductive ingredients, such as carbon of 10 micrometers - 70 micrometers of mean diameters, support catalyst ingredients, such as mean-diameter 10A micrometer-300A Pt and Ru (ruthenium), with sintering, rolling, etc. 10 micrometers - about 100 micrometers are suitable for the thickness of a catalyst bed, and it is processed into magnitude [a little] smaller than the solid-electrolyte

membrane joined.

Electrolyte layer

As for an electrolyte layer, it is desirable to form from the electrolyte ingredient of the same component as a solid-electrolyte membrane. When forming an electrolyte layer in a catalyst bed by heating and application of pressure of a hotpress etc., it is desirable to form an electrolyte ingredient beforehand with a thickness of 1 micrometer - 10 micrometers in the shape of a sheet.

[0010] Formation of the electrolyte layer to a catalyst bed can join a sheet-like electrolyte ingredient to the piece side face of a catalyst bed by giving heating and application of pressure in piles. As the junction approach, a hotpress is applicable. In addition, an electrolyte layer can be formed also by the plasma polymerization as the following examples explain it. More than the glass transition temperature of an electrolyte ingredient, it is appropriate for junction of a catalyst bed and an electrolyte ingredient under the temperature of under decomposition temperature to carry out by applying 30kg/cm² or more the pressure of 500kg/cm² or less, and it is desirable to carry out by 150kg/cm² or more the pressure of 400kg/cm² or less. Drawing 2 is the enlarged drawing showing a part for the joint of a catalyst bed (30) and an electrolyte layer (40). It turns out as a graphic display that an electrolyte ingredient (42) invades between the conductive powder (34) with which catalyst powder (32) was supported, and it is connected by network.

[0011] About a solid-electrolyte membrane (20), it inserts in between so that the electrolyte layer side of a catalyst bed (30) may counter with a solid-electrolyte membrane (20), and heating and application of pressure are given and an electrolyte layer (40) and a solid-electrolyte membrane (20) are joined to the catalyst bed (30) of the couple in which the electrolyte layer (40) was formed (refer to drawing 1). A hotpress can be mentioned as the junction approach. Heating and application-of-pressure conditions can be made into 5kg/cm² or more the pressure of 30kg/cm² or less under the temperature of under decomposition temperature more than the glass transition temperature of an electrolyte ingredient. That what is necessary is just to join an electrolyte layer and a solid-electrolyte membrane so that it may not separate during actuation, since it is not necessary to connect by network like junction in the above-mentioned catalyst bed and an electrolyte layer, a solid-electrolyte membrane can be joined on application-of-pressure conditions weaker than the application-of-pressure conditions which formation of an electrolyte layer took.

[0012] As mentioned above, an electrolyte layer is formed on the surface of a catalyst bed, and the cel for polymer electrolyte fuel cells is produced by joining an electrolyte layer to a solid-electrolyte membrane. In addition, temporarily, at the time of junction in a catalyst bed and an electrolyte layer, with the irregularity of the front face of a catalyst bed (30), since the application-of-pressure conditions at the time of junction to the solid-electrolyte membrane (20) which is an after process also considering breakage (82) as a carrier beam in part are weak, as for a solid-electrolyte membrane (20), an electrolyte layer (40) does not receive breakage.

[0013]

[Example] The catalyst bed was produced in the following ways, the electrolyte layer was formed in the front face of the obtained catalyst bed, it joined to the solid-electrolyte membrane on the electrolyte layer, and the cel for polymer electrolyte fuel cells (this invention cel) was produced. Moreover, for the comparison, it joined to the solid-electrolyte membrane at the catalyst bed which does not form an electrolyte layer, and the cel (reference cell) was produced. The single cel trial was carried out using the produced cel.

[0014] First, the production approach of a catalyst bed is explained.

Catalyst bed

After mixing and filtering CaCO₃ by making Pt support carbon into Binder PTFE (polytetrafluoroethylene) and an ostomy agent, it rolled out and fabricated in the shape of a sheet. Subsequently, it was immersed into 1N-HNO₃, the ostomy agent was removed, and area 2 and the catalyst bed with a thickness of 50 micrometers of 25cm were formed as a porous sheet. Hereafter, all catalyst beds used what was obtained by this production approach.

[0015] The following cels (the invention cels 1-4 and reference cells 1 and 2) were produced using the obtained catalyst bed.

Production of the invention cel 1

The sheet-like electrolyte ingredient (perfluorocarbon-sulfonic-acid film (Du Pont Nafion film), thickness: 5 micrometers) was joined to the front face of the obtained catalyst bed with the hotpress under the temperature of 180 degrees C, and conditions with a pressure of 300kg/cm², and the electrolyte layer was produced. When a part for a joint was observed, the electrolyte layer (40) became the uneven shape of a sheet with a thickness of 1 micrometer - 5 micrometers, it welded (30), and some electrolyte ingredients (42)

had trespassed upon the interior of a catalyst bed (30) (refer to drawing 2). Between one pair of catalyst beds in which the electrolyte layer was formed, the solid-electrolyte membrane with a thickness of 40 micrometers it is thin from the same electrolyte ingredient as an electrolyte layer was inserted, the hotpress was carried out under the temperature of 150 degrees C, and conditions with a pressure of 10kg/cm², the solid-electrolyte membrane was joined to the electrolyte layer, and the invention cel 1 was produced.

Production of the invention cel 2

Except having set to 10 micrometers thickness of the electrolyte layer joined to a catalyst bed, the production approach is the same as the invention cel 1.

Production of the invention cel 3

Except having set to 20 micrometers thickness of the electrolyte layer joined to a catalyst bed, the production approach is the same as the invention cel 1.

Production of the invention cel 4

By the plasma polymerization, the electrolyte layer was formed on the surface of the catalyst bed. As plasma polymerization equipment (90) is shown in drawing 3, one side is connected to a high-frequency power generator (96), and the electrode plate (94) of a couple with which another side was grounded, and (95) are arranged, it is open for free passage to a chamber (93), and raw material charge tubing (97) is connected to the interior of the chamber (93) connected to the vacuum pump (92). Hexafluoropropylene and trifluoro methansulfonic acid were supplied as an electrolyte ingredient (42) from raw material charge tubing (97), having placed the catalyst bed (30) between an electrode plate (94) and (95), having deaerated the inside of a chamber (93) with the vacuum pump (92), and impressing the power of 5W between an electrode plate (94) and (95) by the high-frequency power generator (96). Thereby, the electrolyte membrane with a thickness of about 1.2 micrometers was formed on the surface of the catalyst bed (30). Among one pair of catalyst beds in which the electrolyte layer was formed, the solid-electrolyte membrane was joined by the same approach as the invention cel 1.

[0016] Production of a reference cell 1

The solid-electrolyte membrane with a thickness of 40 micrometers was joined on the same hotpress conditions (the temperature of 150 degrees C, pressure of 10kg/cm²) as the invention cel 1, not forming an electrolyte layer in a catalyst bed.

Production of a reference cell 2

The production approach is the same as a reference cell 1 except having made the hotpress conditions of a solid-electrolyte membrane into the temperature of 150 degrees C, and the pressure of 300kg/cm².

[0017] The obtained invention cels 1-4 and reference cells 1 and 2 were pinched with the carbon paper which gave a water-repellent finish, respectively, and the single cel trial was performed. Trials are the O.C.V. measurement shown below and measurement of the cel electrical potential difference in current density 500 mA/cm², the test condition was not cell temperature [of 80 degrees C], fuel humidification temperature [of 80 degrees C], and oxidizer humidified, H₂ was used as fuel gas and air was used for it as oxidant gas. In addition, the fuel utilization rate made the oxidizer utilization factor 20% 50%.

[0018] When the electrical potential difference (open-circuit voltage: O.C.V.) of each cel when supplying only gas is measured in the condition of not adding the load, as shown in drawing 4, although the invention cels 1-4 and a reference cell 1 all show the high value, the reference cell 2 serves as a low value. Since this had the high application-of-pressure conditions when forming a solid-electrolyte membrane in a catalyst bed, the breakage on a pinhole etc. arises in a solid-electrolyte membrane, and it is considered to be because for leak or an electric short circuit of gas to have occurred. On the other hand, the invention cels 1-4 and a reference cell 1 are considered that there is no breakage in a solid-electrolyte membrane.

[0019] Next, when the cel electrical potential difference in current density 500 mA/cm² is measured, as shown in drawing 4, it turns out that the invention cels 1-4 show the high cel electrical potential difference compared with reference cells 1 and 2. It is because the cel electrical potential difference of reference cells 1 and 2 compared with the invention cels 1-4 and the solid-electrolyte membrane has received breakage as the above-mentioned [low one / a reference cell 2], and although there is no breakage in a solid-electrolyte membrane, since the application-of-pressure conditions of a solid-electrolyte membrane and a catalyst bed are weak, a reference cell 1 is because the network of an electrolyte ingredient and a catalyst bed is not fully performed. The invention cels 1-4 show the high cel electrical potential difference compared with reference cells 1 and 2, because the invention cel has joined the catalyst bed and the electrolyte layer beforehand and the network with an electrolyte ingredient and a catalyst bed is fully performed. Moreover, the junction to the catalyst bed and the solid-electrolyte membrane in which the electrolyte layer was formed is to carry out on weak application-of-pressure conditions, and for a solid-electrolyte membrane not to receive breakage. In

addition, although the cel electrical potential difference is low compared with the invention cels 1, 2, and 4, the thickness of an electrolyte ingredient becomes thick and, as for the invention cel 3, only the part to which this thickened the electrolyte layer shows that oxidizer non-humidified operation is difficult. That is, in performing non-humidified operation, it understands the sum total thickness of an electrolyte layer and a solid-electrolyte membrane that it is desirable to make it thinner than 50 micrometers.

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing the cel for polymer electrolyte fuel cells of this invention.

[Drawing 2] It is the enlarged drawing of the joint of a catalyst bed and an electrolyte layer.

[Drawing 3] It is the explanatory view of plasma polymerization equipment.

[Drawing 4] It is the graph which shows the result of a single cel trial.

[Drawing 5] It is the schematic diagram showing the configuration of a polymer electrolyte fuel cell.

[Drawing 6] It is the sectional view showing the conventional cel for polymer electrolyte fuel cells.

[Description of Notations]

(10) The cel for polymer electrolyte fuel cells

(20) Solid-electrolyte membrane

(30) Catalyst bed

(40) Electrolyte layer

[Translation done.]

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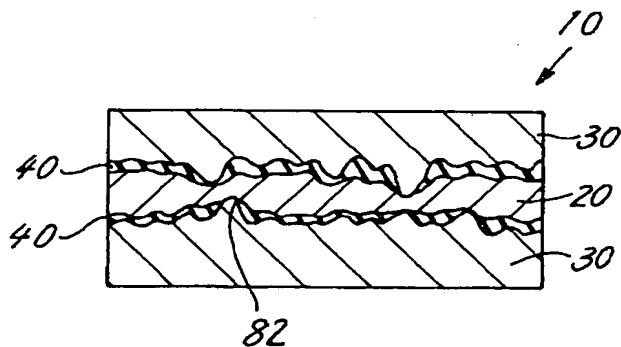
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(54) 【発明の名称】 固体高分子型燃料電池用セル及びその作製方法

(57) 【要約】

【課題】 ピンホールを回避して、固体電解質膜の薄膜化を達成でき、無加湿でも作動可能な固体高分子質型燃料電池用セルを提供する。

【解決手段】 触媒層30と固体電解質膜20との間に、電解質材料からなる電解質層40を形成する。電解質層40は、固体電解質膜20と同じ成分から形成することが望ましい。また、電解質層40と固体電解質膜20の合計厚さは5 μ m ~ 50 μ m とすることが望ましい。



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【特許請求の範囲】

【請求項1】 固体電解質膜(20)の表面に触媒層(30)を配設してなる固体高分子型燃料電池用セルにおいて、触媒層(30)と固体電解質膜(20)の間には、電解質材料からなる電解質層(40)が形成されていることを特徴とする固体高分子型燃料電池用セル。

【請求項2】 電解質層(40)と固体電解質膜(20)の合計厚さは $5\mu\text{m}$ 以上 $50\mu\text{m}$ 以下である請求項1に記載の固体高分子型燃料電池用セル。

【請求項3】 固体電解質膜(20)の表面に触媒層(30)を接合してなる固体高分子型燃料電池用セルの作製方法において、

固体電解質膜(20)との接合側の触媒層(30)面に、電解質材料からなる電解質層(40)を形成し、

触媒層(30)に形成された電解質層(40)と固体電解質膜(20)とを加熱と加圧を行なうことによって接合させることを特徴とする固体高分子型燃料電池用セルの作製方法。

【請求項4】 電解質層(40)は、触媒層(30)とシート状の電解質材料を重ねて配置した後、加熱と加圧して形成される請求項3に記載の固体高分子型燃料電池用セルの作製方法。

【請求項5】 電解質層(40)を触媒層(30)上に形成する工程は、電解質材料のガラス転移温度以上、分解温度未満の温度下にて、 $30\text{kg}/\text{cm}^2$ 以上 $500\text{kg}/\text{cm}^2$ 以下の圧力を加えることによって実施される請求項4に記載の固体高分子型燃料電池用セルの作製方法。

【請求項6】 電解質層(40)を触媒層(30)上に形成する工程は、電解質材料のガラス転移温度以上、分解温度未満の温度下にて、 $150\text{kg}/\text{cm}^2$ 以上 $400\text{kg}/\text{cm}^2$ 以下の圧力を加えることによって実施される請求項4に記載の固体高分子型燃料電池用セルの作製方法。

【請求項7】 電解質層(40)は、触媒層(30)の表面に電解質材料をプラズマ重合させることにより形成される請求項3に記載の固体高分子型燃料電池用セルの作製方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、固体高分子型燃料電池に用いられる固体電解質膜と触媒層からなるセルに関するものであり、具体的には固体電解質膜の薄膜化を達成でき、無加湿でも作動可能なセルに関するものである。

【0002】

【従来の技術】固体高分子型燃料電池(70)は、図5に示すように、イオン導電性であってプロトンを移動させる固体電解質膜(20)の両面に電極(燃料極(72)と空気極(75))が形成されたセル(10)を、燃料極側の燃料室(73)と、空気極側の酸化剤室(76)によって挟んだユニットから構成される。ユニットの燃料室(73)にはメタンガス、

都市ガスなどを改質した水素リッチ燃料ガスが供給され、酸化剤室(76)には空気などの酸素を含む酸化剤ガスが供給される。燃料極(72)では、燃料ガス中の水素ガスが $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ の反応によってプロトンと電子が生成され、プロトンは固体電解質膜(20)を通して空気極(75)に向かい、電子は外部回路(78)に流れる。空気極(75)では、酸化剤ガス中の酸素と、固体電解質膜(20)を通して移動したプロトン及び、外部回路(78)を通して流入した電子が、 $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ の反応により、水を生じると共に、起電力を発生する。

【0003】固体電解質膜の表面に形成される電極(72)(75)は、一般にカーボン粒子などの導電性材料にPtなどの触媒材料を担持させて成形した多孔性の触媒層(30)によって構成される。供給ガスの反応は、電解質材料、導電性材料及び触媒材料が同時に存在する界面が反応点となる。このため、反応点をセル上に多数存在させて、電解質材料、導電性材料及び触媒材料をネットワーク化させることが反応促進に重要となる。そこで従来、セルは、導電性材料と触媒材料からなる触媒層の間に固体電解質膜を挟んでホットプレスすることによって作製されていた。

【0004】固体電解質膜のイオン導電率は、雰囲気中の水分濃度と固体電解質膜の膜厚に著しく依存する。雰囲気中の水分濃度が低いと膜抵抗が増大し、イオン導電率が低下する。しかしながら、膜を湿潤させるには、供給ガスを加湿するなど加湿のための手段が必要となり、固体高分子型燃料電池の大型化、発電効率の低下に繋がる。一方、固体電解質膜の膜厚を薄くすると膜中の水分移動が容易になり、低加湿あるいは無加湿で作動させることができる。また、膜抵抗が小さくなり、セル電圧を向上させることができる。このため、固体電解質膜の薄膜化が進められている。

【0005】

【発明が解決しようとする課題】固体電解質膜の薄膜化を実現する際に、 $50\mu\text{m}$ 以下の薄い固体電解質膜を、触媒層の間に挟んでホットプレスを行なうと、図6に示すように、触媒層(30)の表面の凹凸によって、固体電解質膜(20)が突き破られてピンホール(80)が発生することがあった。固体電解質膜(20)は、プロトンの移動を許容すると共に、燃料ガスと酸化剤ガスが混じるのを防ぐ役割を果たさねばならない。しかし、固体電解質膜(20)にピンホールがあると、供給ガスがリークしやすくなり、望ましくない。加えて、ピンホールを介して燃料極と空気極がショートし、電池の性能低下を引き起こす原因にもなっていた。ピンホールなどの発生を阻止するために、ホットプレスの条件を弱めると、逆に触媒層(30)と固体電解質膜(20)のネットワーク化が不十分となる問題があった。

【0006】本発明の目的は、ピンホールを回避して固体電解質膜の薄膜化を達成でき、無加湿でも作動可能な

固体高分子質型燃料電池用セルを提供することである。

【0007】

【課題を解決するための手段】上記課題を解決するために、本発明の固体高分子質型燃料電池用セル(10)は、触媒層(30)と固体電解質膜(20)との間に、電解質材料からなる電解質層(40)を形成したものである。電解質層(40)は、固体電解質膜(20)と同じ成分から形成することが望ましく、電解質層(40)の厚さは、固体電解質膜(20)よりも薄くすることが望ましい。電解質層(40)は、固体電解質膜(20)との接合側の触媒層(30)の面に形成される。電解質層(40)を形成する方法として、触媒層(30)と、シート状の電解質材料を重ねて配置した後、加熱と加圧を行なう方法を挙げることができる。また、電解質層(40)を形成する別の方法として、触媒層(30)の表面に電解質材料をプラズマ重合させる方法を挙げることができる。電解質層(40)を触媒層(30)に形成した後、触媒層(30)上の電解質層(40)と固体電解質膜(20)とを加熱と加圧によって接合させて、固体高分子質型燃料電池用セル(10)が作製される。

【0008】

【作用及び効果】触媒層(30)に、予め電解質層(40)を形成し、電解質材料、導電性材料及び触媒材料が同時に存在する界面を形成しているため、電解質層(40)の形成された触媒層(30)と、固体電解質膜(20)を接合するときには、弱い加圧条件で固体電解質膜(20)を接合させることができ、固体電解質膜(20)が触媒層(30)によって突き破られることがない。つまり、電解質材料、導電性材料及び触媒材料からなる界面を多数形成しつつ、固体電解質膜(20)の損傷を防ぐことができる。固体電解質膜(20)が損傷を受けることがないから、固体電解質膜(20)を薄膜化しても、ガスのリークや電気的なショートが生じない。また、固体電解質膜(20)の薄膜化を達成することにより、無加湿雰囲気下での作動も可能となる。仮に、固体電解質膜(20)又は電解質層(40)が損傷を受けても、固体電解質膜(20)の上を触媒層(30)側の電解質層(40)が覆っており、固体電解質膜(20)と電解質層(40)の損傷位置とは一致しないから、ピンホールの貫通は起こらない。

【0009】

【発明の実施の形態】本発明の固体高分子質型燃料電池用セルの作製方法の一実施形態について説明する。まず、以下の固体電解質膜、触媒層及び電解質層を準備する。

固体電解質膜

固体電解質膜は、パーフルオロカーボンスルホン酸、スチレンジビニルベンゼンスルホン酸などの電解質材料から形成することができる。固体電解質膜の厚さは、 $5\mu\text{m}\sim 40\mu\text{m}$ とすることが望ましい。また、固体電解質膜の大きさは、作製される固体高分子質型燃料電池の性能に合わせて適宜選択することができる。なお、無加湿で固体高分子質型燃料電池を作動させる場合には、電

解質材料の厚さを薄くする必要があるため、固体電解質膜と固体電解質膜の片面又は両面に接合される電解質層との合計厚さを $5\mu\text{m}$ 以上 $50\mu\text{m}$ 以下とすることが望ましい。

触媒層

触媒層は、平均粒径 $10\mu\text{m}\sim 70\mu\text{m}$ のカーボンなどの導電性材料に、平均粒径 $10\text{\AA}\mu\text{m}\sim 300\text{\AA}$ のPt、Ru(ルテニウム)などの触媒材料を担持させた粉末を、結着剤などと共に焼結、圧延等によって成形した多孔質の薄板によって形成することができる。触媒層の厚さは、 $10\mu\text{m}\sim 100\mu\text{m}$ 程度が適当であり、接合される固体電解質膜より若干小さい大きさに加工される。

電解質層

電解質層は、固体電解質膜と同じ成分の電解質材料から形成することが望ましい。触媒層に電解質層をホットプレスなどの加熱及び加圧によって形成する場合には、電解質材料を予め厚さ $1\mu\text{m}\sim 10\mu\text{m}$ のシート状に形成しておくことが望ましい。

【0010】触媒層への電解質層の形成は、触媒層の片側面にシート状の電解質材料を重ねて、加熱及び加圧を施すことによって接合することができる。接合方法として、ホットプレスを適用することができる。なお、電解質層は、以下の実施例にて説明するとおり、プラズマ重合によっても形成することができる。触媒層と電解質材料の接合は、電解質材料のガラス転移温度以上、分解温度未満の温度下にて、 $30\text{kg}/\text{cm}^2$ 以上 $500\text{kg}/\text{cm}^2$ 以下の圧力を加えることによって実施することが適当であり、 $150\text{kg}/\text{cm}^2$ 以上 $400\text{kg}/\text{cm}^2$ 以下の圧力で実施することが望ましい。図2は、触媒層(30)と電解質層(40)との接合部分を示す拡大図である。図示のとおり、触媒粉末(32)が担持された導電性粉末(34)の間に、電解質材料(42)が侵入してネットワーク化されていることがわかる。

【0011】電解質層(40)が形成された一対の触媒層(30)と、固体電解質膜(20)について、触媒層(30)の電解質層側が固体電解質膜(20)と対向するように間に挟んで、電解質層(40)と固体電解質膜(20)を、加熱及び加圧を施し接合する(図1参照)。接合方法として、ホットプレスを挙げることができる。加熱及び加圧条件は、電解質材料のガラス転移温度以上、分解温度未満の温度下にて、 $5\text{kg}/\text{cm}^2$ 以上 $30\text{kg}/\text{cm}^2$ 以下の圧力とすることができる。電解質層と固体電解質膜は、作動中に剥がれることがないように接合するだけでよく、上記触媒層と電解質層との接合のようにネットワーク化を行なわなくてよいので、電解質層の形成に要した加圧条件よりも、弱い加圧条件で固体電解質膜を接合させることができる。

【0012】上記のように、触媒層の表面に電解質層を形成し、電解質層を固体電解質膜と接合することによって固体高分子質型燃料電池用のセルが作製される。な

お、仮に触媒層と電解質層との接合時に、電解質層(40)が、触媒層(30)の表面の凹凸によって一部損傷(82)を受けたとしても、後工程である固体電解質膜(20)との接合時の加圧条件は弱いため、固体電解質膜(20)は損傷を受けることがない。

【0013】

【実施例】以下の要領にて触媒層を作製し、得られた触媒層の表面に電解質層を形成し、電解質層の上に固体電解質膜と接合して固体高分子質型燃料電池用セル(本発明セル)を作製した。また、比較のために、電解質層を形成しない触媒層に固体電解質膜と接合してセル(比較セル)を作製した。作製されたセルを用いて単セル試験を実施した。

【0014】まず、触媒層の作製方法について説明する。

触媒層

Pt担持カーボンを結着剤PTFE(ポリテトラフルオロエチレン)及び造孔剤としてCaCO₃を混合、ろ過した後、圧延しシート状に成形した。ついで、1N-HNO₃中に浸漬して造孔剤を除去し、多孔性のシートとして、面積25cm²、厚さ50μmの触媒層を形成した。以下、触媒層は、すべてこの作製方法により得られたものを使用した。

【0015】得られた触媒層を用いて、以下のセル(発明セル1~4及び比較セル1、2)を作製した。

発明セル1の作製

得られた触媒層の表面にシート状の電解質材料(パーフルオロカーボンスルホン酸膜(デュポン社製 Nafion 膜)、厚さ: 5μm)を温度180℃、圧力300kg/cm²の条件下でホットプレスによって接合し、電解質層を作製した。接合部分を観察したところ、電解質層(40)は、厚さ1μm~5μmの不均一なシート状となって触媒層(30)に溶着しており、電解質材料(42)の一部が触媒層(30)の内部に侵入していた(図2参照)。電解質層を形成した1対の触媒層の間に、電解質層と同じ電解質材料からなる厚さ40μmの固体電解質膜を挟んで、温度150℃、圧力10kg/cm²の条件下でホットプレスし、電解質層と固体電解質膜を接合して発明セル1を作製した。

発明セル2の作製

触媒層に接合する電解質層の厚さを10μmとしたこと以外は、作製方法は発明セル1と同じである。

発明セル3の作製

触媒層に接合する電解質層の厚さを20μmとしたこと以外は、作製方法は発明セル1と同じである。

発明セル4の作製

プラズマ重合によって、触媒層の表面に電解質層を形成した。プラズマ重合装置(90)は、図3に示すごとく、真空ポンプ(92)に接続されたチャンバー(93)の内部に、一方が高周波電力発生器(96)に接続され、他方がアースさ

れた一対の電極板(94)(95)を配置したものであり、チャンバー(93)に連通して原料投入管(97)が接続されている。電極板(94)(95)の間に触媒層(30)を置き、真空ポンプ(92)によりチャンバー(93)内を脱気し、高周波電力発生器(96)によって電極板(94)(95)間に5Wの電力を印加しながら、原料投入管(97)から電解質材料(42)として、ヘキサフルオロプロピレンとトリフルオロメタンスルホン酸を供給した。これにより、触媒層(30)の表面に厚さ約1.2μmの電解質膜が形成された。電解質層の形成された1対の触媒層間に、発明セル1と同様の方法で固体電解質膜を接合した。

【0016】比較セル1の作製

触媒層に電解質層を形成しないまま、発明セル1と同じホットプレス条件(温度150℃、圧力10kg/cm²)で厚さ40μmの固体電解質膜を接合した。

比較セル2の作製

固体電解質膜のホットプレス条件を温度150℃、圧力300kg/cm²とした以外、作製方法は比較セル1と同じである。

【0017】得られた発明セル1~4と、比較セル1、2を、それぞれ撥水处理を施したカーボンペーパーで挟み、単セル試験を行った。試験は、以下に示すO.C.V.測定と、電流密度500mA/cm²でのセル電圧の測定であって、試験条件は、電池温度80℃、燃料加湿温度80℃、酸化剤無加湿であり、燃料ガスとしてH₂、酸化剤ガスとして空気をを用いた。なお、燃料利用率は50%、酸化剤利用率は20%とした。

【0018】負荷を加えていない状態で、ガスのみを供給したときの各セルの電圧(開回路電圧: O.C.V.)を測定したところ、図4に示すように、発明セル1~4及び比較セル1は、何れも高い値を示しているが、比較セル2は低い値となっている。これは、触媒層に固体電解質膜を形成したときの加圧条件が高かったため、固体電解質膜にピンホールなどの損傷が生じて、ガスのリークまたは電気的なショートが発生しているためであると考えられる。一方、発明セル1~4及び比較セル1については、固体電解質膜には損傷はないと考えられる。

【0019】つぎに、電流密度500mA/cm²でのセル電圧を測定したところ、図4に示すように、発明セル1~4は、比較セル1、2に比べて高いセル電圧を示していることがわかる。比較セル1、2のセル電圧が、発明セル1~4に比べて低いのは、比較セル2は前述のとおり固体電解質膜が損傷を受けているためであり、比較セル1は固体電解質膜に損傷はないけれども、固体電解質膜と触媒層との加圧条件が弱いため、電解質材料と触媒層のネットワーク化が十分に行なわれていないためである。発明セル1~4が、比較セル1、2に比べて高いセル電圧を示しているのは、発明セルは、予め触媒層と電解質層を接合しており、電解質材料と触媒層とのネットワーク化が十分に行われているためである。また、

電解質層を形成した触媒層と固体電解質膜との接合は、弱い加圧条件で実施しており、固体電解質膜が損傷を受けることがないためである。なお、発明セル3は、発明セル1、2及び4に比べてセル電圧が低くなっているが、これは、電解質層を厚くした分だけ、電解質材料の厚さが厚くなり、酸化剤無加湿運転が困難となっていることを示している。つまり、無加湿運転を行なう場合には、電解質層と固体電解質膜との合計厚さは、 $50\mu\text{m}$ より薄くすることが望ましいことがわかる。

【図面の簡単な説明】

【図1】本発明の固体高分子質型燃料電池用セルを示す断面図である。

【図2】触媒層と電解質層との接合部の拡大図である。

【図3】プラズマ重合装置の説明図である。

【図4】単セル試験の結果を示すグラフである。

【図5】固体高分子質型燃料電池の構成を示す概略図である。

【図6】従来の固体高分子質型燃料電池用セルを示す断面図である。

【符号の説明】

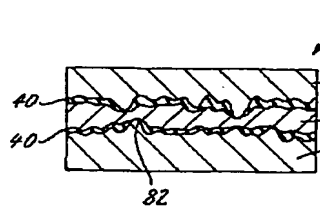
(10) 固体高分子質型燃料電池用セル

10 (20) 固体電解質膜

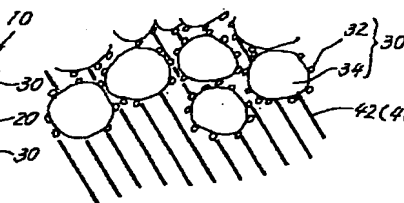
(30) 触媒層

(40) 電解質層

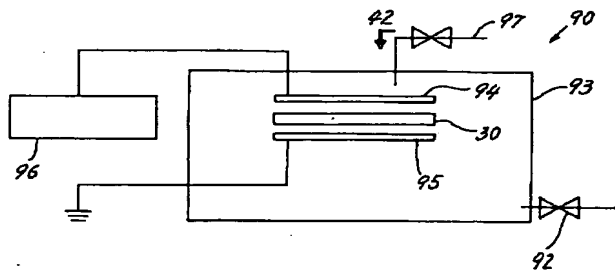
【図1】



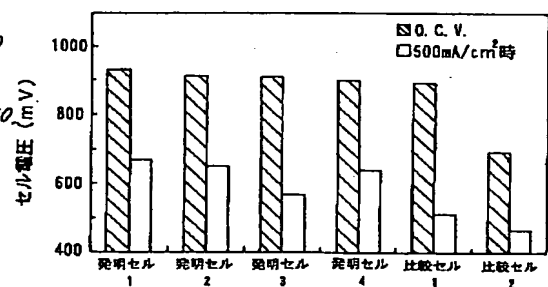
【図2】



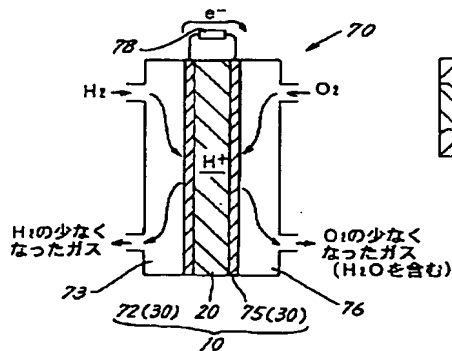
【図3】



【図4】



【図5】



【図6】

